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SYNTHESIS OF NOVEL WO₃/ZrSiO₄ CATALYSTS FOR DEHALOGENATION OF HALOGENATED HYDROCARBONS

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Abstract

This research aimed to develop a novel catalyst based on WO₃/ZrSiO₄ system for halogenated hydrocarbons processing. The production method of this catalyst involved extrusion and as such was simplified compared to thermo-chemical synthesis routes. It had a reduced number of process stages and a lower environmental impact at the same time. In order to examine the phase composition of the catalyst after sintering at 800 °C, the XRD analysis was carried out. The catalyst was then tested in chlorodifluoromethane dehalogenation process on laboratory scale at temperatures of 300, 400 and 500 °C in the presence of water vapor. Catalyst achieves high dehalogenation efficiencies of 88.6, 95.9, and 99.5 % for each of the process temperatures, respectively. Obtained results are in the range with those achieved by using thermo-chemically prepared dehalogenation catalysts.

Keywords: catalyst; Tungsten (VI) oxide; Zirconium (IV) silicate; halogenated hydrocarbons; cooling equipment recycling.

Introduction

The present research aimed to develop a novel WO₃/ZrSiO₄ catalyst for treatment of halogenated hydrocarbons and to produce it by a method more simplified in comparison with the conventional catalyst synthesis routes. Many halogenated hydrocarbons, such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and others, exhibit a pronounced harmful effect on the ozone layer. Those compounds have a wide range of industrial application, and among other uses, they serve as refrigerants and as blowing agents for thermal insulating foams within cooling equipment. Before such equipment and foams are recycled or disposed of, halogenated hydrocarbons

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have to be safely extracted and recovered or destroyed [1]. The current state of scientific research shows that gas phase catalytic dehalogenation is one of the recommended technologies for the destruction of those compounds. It includes hydrogenation, oxidation, and hydrolysis, whereby catalytic hydrolysis is the most favorable from a thermodynamic point of view [1, 2]. Hydrolysis as a process requires simple equipment, mainly a reactor with a packed catalyst bed and a hydrogen source. The catalyst directly enables the reaction of halogenated hydrocarbons with hydrogen by weakening the bonds between carbon and halogen elements [2, 3].

The most common dehalogenation catalysts are based on mixed metal oxides and a certain amount of platinum group metals. The main active component is ZrO_2 and/or TiO_2 , and others are WO_3 , V_2O_5 , SnO_2 and Pd, Pt or Rh [4-7]. Although catalysts with noble metals are highly active and enable a complete decomposition of halogenated hydrocarbons [3], efficient CFC-12 treatment systems can only contain oxides. Such oxides include as an example, $\text{TiO}_2/\text{ZrO}_2$ [2], WO_3/ZrO_2 [7], WO_3/TiO_2 [8] and WO_3/SnO_2 [8], that are types of solid acids which prevents their deactivation, and their acidity is additionally increased when promoted with SO_4^{2-} ions [6, 8-10]. Catalyst $\text{TiO}_2/\text{ZrO}_2$ grants complete CFC-12 dehalogenation, and its deactivation is prevented by treatment with aqueous solution of H_2SO_4 that has a concentration of 96 vol.% [2]. Among WO_3/ZrO_2 catalysts tested in the same process, the highest initial activity is achieved with approximately 17 wt.% of WO_3 , but the catalyst deactivates in time. When WO_3/ZrO_2 system contains about 13 wt.% of WO_3 , it also provides a high CFC-12 dehalogenation efficiency, about 97 %, and exhibits a pronounced deactivation resistance during exploitation [7].

Thermo-chemical synthesis routes are commonly used to produce catalysts with the following stages: impregnation, precipitation, co-precipitation, sol-gel and other, or by their combination. Process stages of those routes involve: 1) preparing solutions of chemicals used for catalyst synthesis; 2) preparing precursors for catalysts by adjusting solution pH values or by enabling other chemical reactions in the solutions; 3) filtration of formed precursor precipitates; 4) drying of the precursors or, depending on a route, multiple rinsing, filtration, and drying; 5) calcination in a suitable atmosphere to obtain catalyst in the form of powder; 6) supplementary treatment of the catalyst to form the desired shape (pressing, pelletizing, monolithic honeycombs washcoating and other). Despite obtaining high-performance catalysts, thermo-chemical synthesis routes are complex from a cost-effective point of view: they last from 30 to 50 hours or even up to a few days and require large amounts of complex chemical composition solutions [2, 4-10]. Hence, it is highly desirable to simplify the catalyst production processes by reducing the number of process stages and in conjunction also achieve a lower environmental impact when compared with the thermo-chemical synthesis routes [11-13].

In this research, $\text{WO}_3/\text{ZrSiO}_4$ catalyst was successfully developed and synthesized by extrusion. It exhibited high activity in the chlorodifluoromethane (CFC-22) dehalogenation. Together with the reduced impact on the environment, commercially available materials that do not include noble metals significantly improve the overall economic aspect of the production process.

Experimental

To synthesize the catalyst, the following commercially available starting powders were used: WO_3 , ZrSiO_4 , and kaolin clay (Sigma-Aldrich, pro analysis). An aqueous solution of H_2SO_4 with concentration of 16 vol.% was used as a liquid phase.

First, a dry mixture of starting powders containing 17.86 wt.% WO_3 , 78.57 wt.% ZrSiO_4 and 3.57 wt.% clay was prepared and homogenized in a ball mill. The content of those components was selected by research conducted by *Hua et al.* [7] due to catalyst composition similarity. The low-temperature sintering kaolin clay serves as a binder and enables catalyst shaping. After homogenization, 16 % H_2SO_4 solution was added to the powder mixture and stirred to prepare a thick paste, which contained about 15 wt.% of the solution. The paste was aged in order to enable even distribution of the liquid phase. Cylinders prepared by extruding of the paste and cutting were dried in two stages to avoid cracking during sintering. Technological scheme of the production process is presented in Fig. 1 and the final product is shown in Fig. 2.

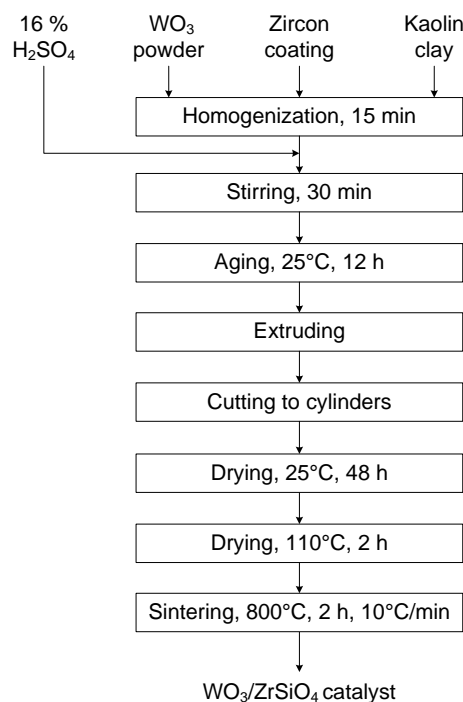
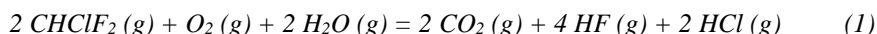


Fig. 1. Technological scheme of the $\text{WO}_3/\text{ZrSiO}_4$ based catalyst production process.

Characterization of the synthesized catalyst has included the X-ray diffraction (XRD) analysis to examine its phase composition after sintering at 800 °C. The XRD analysis was performed on the Roentgen diffractometer “PHILIPS”, model PW-1710, with a curved graphite monochromator and a scintillation counter. Intensities of the diffracted $\text{CuK}\alpha$ Roentgen radiation ($\lambda=1,54178 \text{ \AA}$) were measured at room temperature at intervals of $0.02^\circ 2\theta$ and for a time of 1 s, in the range from 4 to $70^\circ 2\theta$. Roentgen tube

was exposed to a voltage of 40 kV and a current of 30 mA, while the slots for directing the diffracted beam were 1° and 0.1 mm. Diffractogram of the sintered catalyst sample is presented in Fig. 3.

Catalyst functionality was tested in CFC-22 dehalogenation in the presence of water vapor. The process reaction occurs according to the chemical equation (1) [5]:



The experiment was carried out in a tubular quartz reactor with a packed catalyst bed, as presented in Fig. 4. Catalyst specific surface area of $0.66 \text{ [m}^2/\text{kg]}$ was calculated by dividing the specific surface area of particles in the packed bed $[\text{m}^2/\text{m}^3]$ with the bulk density of the packed bed $[\text{kg}/\text{m}^3]$. Inlet gas stream mixture contained 0.08 % CFC-22 diluted in oxygen and water vapor in a quantity of at least twice than CFC-22 quantity in order to ensure complete reaction. Ratio of catalyst specific surface area and unit CFC-22 flow rate was set to about $130 \text{ [m}^2] \text{ catalyst} / 1 \text{ [m}^3/\text{h]} \text{ CFC-22}$. The efficiency of the dehalogenation process was determined by measuring the total organic carbon concentration (TOC) and by subsequent calculation according to the equation (2):

$$\varepsilon = (1 - C_{out}/C_0) \times 100 \quad (2)$$

where:

C_{out} – TOC concentration in outlet gas mixture after dehalogenation reaction,

C_0 – reference TOC concentration before the dehalogenation reaction,

ε – catalytic dehalogenation process efficiency (%).

Results and discussion

The catalyst was prepared by the extrusion method, which is considerably simplified in comparison with thermo-chemical processes in regard to the elimination of following stages: 1) preparation of chemically complex solutions, 2) formation of semi-products for catalysts synthesis from solutions, 3) separation of the semi-products, 4) additional treatment of semi-products that involves rinsing, filtration, and drying. Photograph of the prepared catalyst is presented in Fig. 2.



Fig. 2. Catalyst cylinders obtained by extrusion and sintered at 800°C .

Diffraction pattern of the sintered catalyst (Fig. 3) shows the presence of two main phases – ZrSiO_4 and monoclinic WO_3 . That composition corresponds to the previously determined system for dehalogenation processes. Obtained results indicate that no contamination in the catalyst production process has occurred, or if any undesirable phases were present, they were below the detection limit. Furthermore, low-temperature melting phases were not detected, which is very significant because the presence of such phases could impair catalyst activity in several ways. For example, the activity can be decreased if an inactive compound is present in catalyst while dehalogenation occurs or if a low-temperature melting phase coats catalytically active particles and prevents contact between gases and these particles.

Results of the CFC-22 dehalogenation at three different temperatures are presented in Table 1.

It can be noted that process efficiency increased with an increase in temperature, with the highest achieved value of 99.5 % at 500 °C.

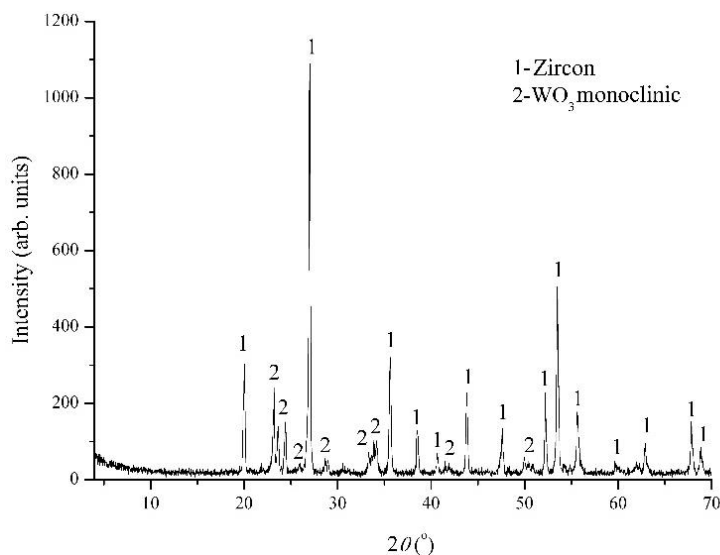


Fig. 3. Diffraction pattern of the catalyst sample sintered at 800 °C

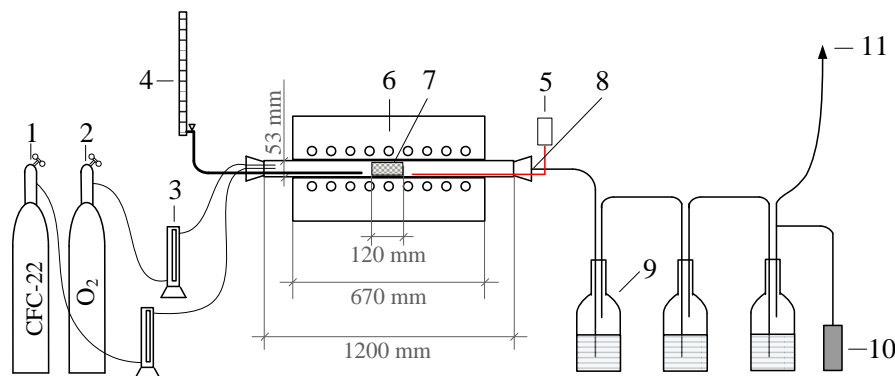


Fig. 4. Experiment set-up for catalytic dehalogenation of CFC-22: 1 – CFC-22 under pressure, 2 – oxygen under pressure, 3 – rotameter, 4 – burette with water, 5 – thermocouple, 6 – electric resistant furnace, 7 – catalyst packing, 8 – measuring point during a cold probe performing, 9 – wash bottle with water, 10 – device for TOC measuring, 11 – measuring point during the catalyst activity test.

Table 1. Results of the CFC-22 dehalogenation process.

Process temperature, °C	Process efficiency, %
300	88.6
400	95.9
500	99.5

By the obtained results, it was concluded that the synthesized $\text{WO}_3/\text{ZrSiO}_4$ catalyst exhibited activity comparable to those obtained by using thermo-chemically prepared catalysts, including systems that contained noble metals. The production process was notably simplified compared with thermo-chemical synthesis routes because excess process stages were eliminated and, consequently its environmental impact was reduced. Therefore, research in the future will include further development of the catalyst production technology in order to apply it to a semi-industrial scale. The aim will be to eliminate the emission of a mixture of various halogenated hydrocarbons into the environment during mechanical recycling of cooling equipment.

Conclusions

In this research, a novel $\text{WO}_3/\text{ZrSiO}_4$ catalyst for treatment of halogenated hydrocarbons was developed. The production process was considerably simplified by replacing the thermochemical synthesis routes with the extrusion method thus reducing the number of process stages by four. Laboratory scale testing of catalytic performance was carried out in dehalogenation of chlorodifluoromethane at temperatures of 300, 400 and 500 °C. Higher dehalogenation efficiencies were achieved with the temperature increase and are in the range of 88.6 to 99.5 %, which is on par with conventionally synthesized catalysts.

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References

- [1] S. Devotta, A. Finkelstein, L. Kuijpers, Montreal Protocol On Substances that Deplete the Ozone Layer, Report of the Task Force on Destruction Technologies, TUE Eindhoven, Netherlands, 2002.
- [2] S.Y. Lai, W. Pan, C. Fai Ng: Appl Catal, B, 24 (2000) 207–217.
- [3] B. Huang, C. Lei, C. Wei, G. Zeng: Environ Int, 71 (2014) 118–138.
- [4] T. Karnaukhov, A. Vedyagin, I. Mishakov, A. Bedilo, A. Volodin: Mater Sci Forum, 917 (2018) 157–161.
- [5] G. R. Lester, US 5176897 A, <http://www.google.com/patents/US5176897>
- [6] H. Zhang, C. Fai Ng, S. Yin Lai: Appl Catal, B, 55 (2005) 301–307.
- [7] W. Hua, F. Zhang, Z. Ma, Y. Tang, Z. Gao: Catal Lett, 65 (2000) 85–89.
- [8] Z. Ma, W. Hua, Y. Tang, Z. Gao: J Mol Catal A: Chem, 159 (2000) 335–345.
- [9] M. Zhen, H. Wei-Ming, T. Yi, G. Zi: Chin J Chem, 18 (2000) 341–345.
- [10] S. Kanno, H. Kawagoshi, A. Kato, T. Arato, H. Yamashita, S. Azuhata, S. Tamata, S. Ikeda, T. Yasuda, US 5877391 A, <http://www.google.com/patents/US5877391>
- [11] B. Agarski, V. Nikolić, Ž. Kamberović, Z. Anđić, B. Kosec, I. Budak: J Cleaner Prod, 162 (2017) 7–15.
- [12] M. Sokić, Ž. Kamberović, V. Nikolić, B. Marković, M. Korać, Z. Anđić, M. Gavrilovski: Sci World J (2015).
- [13] M.F. Mohd Na'aim, R.M. Ramli, N.A. Mohd Zabidi: Metall Mater Eng, 24 (2018) 1–16.



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